

# Axiomatic Foundations of Thermostatistics

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## Abstract

A realistic and objective axiomatic formulation of Thermostatistics for composite systems is presented. The main feature of our axiomatics is that it is free of empirical definitions. In particular, the basic concepts of the theory, such as those of entropy, heat and temperature, are characterized only by the axiomatic basis and the theorems derived from it. We also show that the concept of (quasi)static process does not belong to the body of Thermostatistics.

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## 1 Introduction

Throughout the history of science there have been many attempts to formulate a consistent axiomatization of Thermodynamics. Although the most widely known example is the work of Carathéodory [1], the first attempt, by J. Gibbs, dates back to 1875 (For historical references, see Truesdell [2]). Gibbs took at first energy, entropy, and absolute temperature as primitive concepts, and later, in 1901, he tried to find a statistical basis for the concept of entropy. Many axiomatic formulations of Thermodynamics have been developed since then. In most of the cases the aim was to obtain a better understanding of the concept of entropy. Some “operational definition” (formulated in terms of measurable quantities) of entropy is at the heart of many of these attempts. For instance, Rastall [3] emphasised that “The advantage of our formalism is that it gives a more immediate insight into the meaning of entropy and temperature.” Another example is Tisza [4], who put the theory of Gibbs in an axiomatic format. Several authors [5, 6, 7, 8, 9, 3] presented modern versions of Carathéodory’s axiomatization<sup>1</sup>. These and many other related works have (mistakenly, as we shall see) led to the certainty that Thermodynamics rests on solid foundations.

This approach to the axiomatization of Thermodynamics is based on the derivation of the entropy function under certain assumptions. Some authors

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<sup>1</sup>A critical analysis of the original formulation of Carathéodory can be found in [2].

[5, 6, 7, 8, 9, 3] base their work on Caratheodory's axiom of adiabatic inaccessibility, together with topological postulates on the set of thermodynamic states. Zeleznik [10] postulates that Thermodynamics has an algebraic structure and identifies the entropy as a purely mathematical concept. The recent work of Lieb and Yngvason [11] is surely the most elaborated along these lines. They derive the entropy function from certain axioms that satisfy the order relation of adiabatic accessibility among equilibrium states.

Unfortunately, all these axiomatizations are pervaded by the philosophical tenet known as operationism. According to it, the factual meaning of scientific constructs is specified only through measurable quantities or processes that relate them. A typical example is that of temperature. We read in Ref. [12] that " $T$  is a universal function of the temperature of the system as recorded by measuring some arbitrary property like electrical resistance". Many scientists are firmly convinced of the need of this type of definition. For instance, Ref. [13] maintains that "In physical science, a concept is defined by experimental instruction. For quantitative concepts, the instruction must lead to a Dedekind cut, *i.e.* to a measurement. It is necessary and sufficient for the definition of a property  $P$  that the prescribed experimental procedures decides whether the value..." . In spite of this support, any axiomatics constructed on the operationist basis inevitably leads to inconsistencies, because operationalism fails to realize the difference between the measurement of a magnitude (a fact) and the definition of a concept (a purely conceptual process). It is true that Thermodynamics, as any other phenomenological theory, involves and interrelates observational variables. However, the definition of these cannot be reduced to laboratory operations. Moreover, as we shall see below several concepts with no counterpart in the physical world play an important role in Thermodynamics (for example, that of state)<sup>2</sup>.

In many of these formulations, guided by empiricist philosophies, heat is considered as a concept that should not be defined because it cannot be measured. Accordingly, Lieb and Yngvason [11] state that "Another mysterious quantity is 'heat'. No one has ever seen heat, nor will it ever be seen, smelled or touched... There is no way to measure heat flux directly... The reader will find no mention of heat in our derivation of entropy, except as a mnemonic guide." Another author says that "It certainly would not do to say that Thermodynamics deals with 'heat'. The latter has not been defined, and indeed never be explicitly defined at all." [6]. However, Lavoisier and Laplace [15] defined the concept of heat (in the framework of "caloric" theories), and devised accurate methods of measuring heat fluxes. More remarkably, these methods served as the foundation basis of Calorimetry, a branch of Thermodynamics that is essential to research in many areas of science, such as physical chemistry or low-temperature physics. We then take the view that any axiomatization of Thermodynamics must try to define and clarify the concept of heat.

Another important remark is that the distinction between Thermodynamics and Thermostatistics is "something not widely understood even today" [2]. However, we can assert that the main interest of Thermostatistics is the study of the equilibrium states of a system. Consequently, the concept of *process* (in the sense of time evolution of the state of a system) is alien to Thermostatistics. On the other hand, Thermodynamics deals with processes in which a certain

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<sup>2</sup>A complete criticism of operationism can be found in Ref. [14]

property, namely entropy, is produced in an irreversible way. These processes cannot be spontaneously time reversed, and so time plays an important albeit silent rôle in describing the evolution of thermodynamical systems.

We think then that Thermodynamics and Thermostatistics need a revision of their foundations. With this purpose in mind, we shall present here a realistic and objective axiomatization of Thermostatistics. We hope to report more on the subject in a future paper on Thermodynamics. Needless to say, the axiomatic format offers several advantages when compared to other presentations. First, in it all the presuppositions of the theory are made explicit from the beginning. This helps to avoid the intrusion of elements alien to physics (*e.g.*, observers). Second, the identification of the physical referents of the theory can be safely performed. The referents are simply the arguments of the functions that appear in the different statements [16]. Third, the assignation of meaning by means of semantical axioms precludes mistakes that originate in abuse of analogy. Finally, the axiomatic format clarifies the structure of the theory and so it paves the way to the deduction of theorems and the elimination of pseudotheorems.

In order to make contact with previous axiomatics, we must have some criteria to discern between two axiomatic formulations of the same theory. A first noticeable difference originates in the freedom we have on the election of the primitive basis. A second distinguishing feature, which usually goes unnoticed in physics, are the philosophical presuppositions adopted by each axiomatic system. We gave above some of the reasons why operationism, one of the most common tenets among scientists, should be discarded from further consideration in philosophy of science. We shall adopt instead a realistic philosophy [17, 18, 19]. We support realism because, contrary to idealism, we assume that the entities we shall study (*i.e.* the reference class of our axiomatization) exist irrespectively of our sensory experience. Finally, we shall see that our axiomatization is objective, because no subject belongs to the domain of quantification of the bound variables of the theory.

The structure of the paper is the following. In the next section, we give a brief summary of our ontologic presuppositions, which is based on the realistic ontology of Bunge [18, 19]. In Section 3 we present in detail the axiomatic basis of the theory. In Section 4 we show that several important theorems can be derived from our basis. Finally, in the last section we compare our presentation with previous ones, and we discuss our results.

## 2 Ontological Background

Originally, the interest in Thermodynamics arose with the need to understand the transformation of energy by means of thermal machines. A thermal machine is defined as a body composed of several parts placed in a certain order and joined to each other, forming a unit. Contrary to what happens in simpler structures, if two parts are changed in one of these machines, it loses some (or all) of its features as a whole. But the latter is no other than the ontological concept of *system*. In particular, the formulation of Thermostatistics that we shall present here will refer to concrete systems, that is to say, bodies connected to each other in some way. Before giving a brief summary of the general theory of systems we must characterize a few concepts.

The basic concept of the realistic ontology developed in Refs. [18, 19] is

that of *substantial individual*. Substantial individuals can associate to form new substantial individuals, and they differ from the fictional entities called *individuals without properties* precisely in that they have a number of properties in addition to their capability of association. Thus, concrete things are built from substantial individuals  $\xi$  together with their properties  $P(\xi)$ . In short, denoting a thing by  $x$ , then we have:  $x = \langle \xi, P(\xi) \rangle$ <sup>3</sup>. We will assume that any property  $P$  of a thing  $x$  is represented by a mathematical function  $F$ , that is to say  $F \triangleq P$ . We are interested in a formal characterization of a system. Some definitions are needed first.

**D 1 (Physical addition)** *Let  $x$  and  $y$  be two different things. We can form a new thing  $z$  by juxtaposing  $x$  and  $y$ , that is to say:  $z = x \dot{+} y$*

**D 2 (Action)** *A thing  $x$  acts on another thing  $y$  if  $x$  modifies the behavior of  $y$ . ( $x \triangleright y$  :  $x$  acts on  $y$ ). If the action is mutual it is said that they interact ( $x \bowtie y$ ).*

**D 3 (Connection)** *Two things are connected (or bonded) if at least one of them acts on the other.*

In particular, the *bondage* of a set of things  $A \subseteq \Theta$  is the set  $B(A)$  of bonds (or links or connections) among them.

**D 4 (Absolute Composition)** *For every  $x \in \Theta$ , the composition of  $x$  is:*

$$\mathcal{C}(x) = \{y \in \Theta / y \sqsubset x\},$$

where “ $y \sqsubset x$ ” designates “ $y$  is part of  $x$ ”.

**D 5 (Absolute environment)** *The environment of a thing  $x$  is the set of things that are not parts of  $x$  but that are connected with some or all parts of  $x$ , that is*

$$\mathcal{E}(x) = \{y \in \Theta / y \notin \mathcal{C}(x) \wedge (\exists z)(z \in \mathcal{C}(x) \wedge (y \triangleright z \vee z \triangleright y))\}.$$

**D 6 (Absolute structure)** *We will call structure of a thing  $x$  the set of bonds  $\mathcal{L}(x)$  among the components of  $x$  and among  $x$  and the things in its environment.*

A thing composed of at least two coupled components will be called a system. Formally,

**D 7 (System)** *A system  $\sigma$  is a thing composed of at least two different connected things.*

We will adopt here a *minimal* model of system constituted by the ordered triple:

$$\mathcal{S}(\sigma) = \langle \mathcal{C}, \mathcal{E}, \mathcal{L} \rangle.$$

Since in general we shall be dealing with systems composed of other systems, we should keep in mind that a component can also be a system itself. We need then to introduce the notion of *subsystem*:

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<sup>3</sup>The set of all things will be denoted by  $\Theta$ .

**D 8 (Subsystem)** Let  $\sigma$  be a system with  $\langle \mathcal{C}(\sigma), \mathcal{E}(\sigma), \mathcal{L}(\sigma) \rangle$ . Then a thing  $\sigma_i$  is a subsystem of  $\sigma$  ( $\sigma_i \prec \sigma$ ) if and only if:

1.  $\sigma_i$  is a system, and
2.  $(\mathcal{C}(\sigma_i) \subseteq \mathcal{C}(\sigma)) \wedge (\mathcal{E}(\sigma_i) \supseteq \mathcal{E}(\sigma)) \wedge (\mathcal{L}(\sigma_i) \subseteq \mathcal{L}(\sigma))$ .

In particular, Thermostatistics is concerned with only one kind of relationship, namely bond relationships. The bonds among subsystems are called *internal bonds*, while the bonds between the system and their environment are called *external bonds*.

Theoretical physics does not deal with concrete things but with concepts, in particular with conceptual schemes called models. For example, a certain quantity of oxygen is a thing, but in Thermostatistics we shall be concerned with a certain quantity of moles of a given ideal gas, so the real gas is modeled by the ideal gas.

**D 9 (Functional schema)** Let  $\sigma_i$  be a system. A functional schema  $b$  of  $\sigma_i$  is a certain nonempty set  $M$ , together with a finite sequence of mathematical functions  $F_i$  on  $M$ , each one of which represents a property of  $\sigma_i$ . Shortly:

$$b = \langle M, \mathbf{F} \rangle,$$

where

$$\mathbf{F} = \langle F_i / F_i \text{ is a function with domain } M \wedge 1 \leq i \leq p \rangle.$$

Therefore, the thing  $\sigma_i$  will be represented by the functional scheme  $b$ , that is to say  $b \stackrel{\wedge}{=} \sigma_i$ .

**Remark:**

The auxiliary set  $M$  generalizes in ontology the usual physical notion of *reference system*. It can be built as the conceivable state space (see below) of a reference thing  $x_f$ . In thermostatistics, it can be constructed as a particular subset of the state space (see remarks to Ax.7).

As we stated above, real things have properties. A detailed account of the theory of properties is given in Ref. [18]. We shall give here only some useful definitions.

**D 10**  $P \in \mathcal{P} \leftrightarrow (\exists \xi)(\xi \in S \wedge P\xi)$ .

Here  $\mathcal{P}$  is the set of all substantial properties, and  $S$ , the set of substantial individuals. The set of all the properties of a given individual is given by

**D 11**  $P(\xi) = \{P \in \mathcal{P} / P\xi\}$ .

We shall adopt the following classification of properties:

**D 12 (Extensive and intensive properties)** Let  $P$  be a property of a composite system  $\sigma = \sigma_1 \dot{+} \sigma_2$ , such that  $F \stackrel{\wedge}{=} P$ .  $P$  is an extensive property if and only if  $F(\sigma_1 \dot{+} \sigma_2) = F(\sigma_1) + F(\sigma_2)$ . Otherwise, the property  $P$  will be called intensive.

**D 13** Let  $P$  be a property of  $\sigma_i$  in an environment  $\overline{\sigma}_i$ . Then  $\sigma_i$  is open with respect to  $P$  if and only if  $P$  is related to at least one property of things in  $\overline{\sigma}_i$ . Otherwise  $\sigma_i$  is closed regarding  $P$ .

**D 14** A system is closed if and only if it is closed for every  $P \in \mathcal{P}$ .

**Remarks:**

1. Our definition of environment of a system (**D5**) as the set of all the things coupled with the components of the system requires a careful distinction of the different types of connections: internal and external, chemical, mechanical, etc. These connections must be taken from the background theories.
2. Notice that we talk about *relationships* among properties of a thing and *connections* between things since the properties are interdependent but not interacting.

It is natural to assume that all things are in some state (without specifying the type). The state of a system can be characterized as follows:

**D 15 (State function)** Let  $\sigma_i$  be a system modeled by a functional schema  $b = \langle M, \mathbf{F} \rangle$ , such that each component of the function

$$\mathbf{F} = \langle F_1, F_2, \dots, F_p \rangle : M \rightarrow V_1 \times V_2 \times \dots \times V_p$$

represents a property of  $\sigma_i$ . Then, each  $F_i$  is a state function (or state coordinate) of  $\sigma_i$ .  $\mathbf{F}$  is the total state function of  $\sigma_i$  and its value

$$\mathbf{F}(m) = \langle F_1, F_2, \dots, F_p \rangle(m) = \langle F_1(m), F_2(m), \dots, F_p(m) \rangle$$

for any  $m \in M$  it represents the state of  $\sigma_i$  in the representation  $b$ .

**Remarks:**

1. A very important point concerning the notion of state is that according to our definition **D15** every state is a state of some concrete thing. States are concepts that model the properties of a physical system more or less accurately, but the converse is not true: a physical system cannot be conceived as a bundle of properties without physical support.
2. It must be noted that although the ontological concept of *state* was defined in **D15**, it is not the aim of Ontology to specify a particular type of state. More specifically, Thermostatistics only deals with *equilibrium states*, not with *quasiequilibrium states*. We shall see below that these equilibrium states are characterized by a particular value of the state function  $\mathbf{F}$  of the system.

We shall call *conceivable state space* the set formed by the Cartesian product of the range of each of the functions of  $\mathbf{F}$ . This set will be denoted by  $S(\sigma_i)$ .

The states of the system are parametrized by the states of another thing  $x_f$  that qualifies as a reference frame, in the sense that  $M = S(x_f)$ . That is, for

each state  $t \in M$  of the reference frame, the system is in the state  $s = \mathbf{F}(t)$ , where  $\mathbf{F}$  is the state function of the system.

Any restriction on the possible values of the components of  $\mathbf{F}$  and any relationship among them is called a *law statement*. The set of all the law statements involving  $\sigma_i$  will be denoted  $\mathbf{L}(\sigma_i)$ .

**D 16 (Lawful state space)** *The subset of the range of  $\mathbf{F}$  restricted by those law statement in  $\mathbf{L}(\sigma_i)$  will be called the lawful state space of  $\sigma_i$  in the representation  $b$ , and it will be denoted by  $S_{\mathbf{L}}(\sigma_i)$ .*

Every event is really a change of state of a system. If such a change of state is carried out along a curve that characterizes the intermediate states, the change we will call a *transformation* and it will be represented by a curve in the lawful state space of the system.

**D 17 (Lawful transformations)** *Let  $S_L(\sigma_i)$  be the state space of system  $\sigma_i$ . Then the family of lawful transformations of the lawful state space into itself is the set  $G_L$  of functions  $g$  such that:*

$$G_L(\sigma_i) = \{g : S_L(\sigma_i) \rightarrow S_L(\sigma_i) \wedge g \text{ is compatible with the laws of } \sigma_i\}$$

The transformation with starting point  $\varphi$  and ending point  $\varphi'$  (with  $\varphi$  and  $\varphi' \in S_L(\sigma_i)$ ) will be represented by the triple  $\langle \varphi, \varphi', g \rangle$  where  $g \in G_L(\sigma_i)$  and  $\varphi' = g(\varphi)$ .

In the next section we will give an axiomatic presentation of Thermostatistics based on this ontological background. Supplementary comments were added where we felt some elucidation was needed.

## 3 Axiomatics

### 3.1 Formal Background

1. Bivalent logic.
2. Formal semantics.
3. Mathematical analysis.

### 3.2 Material Background

1. Macroscopic physics: classical mechanics, electromagnetism, etc.
2. Chemistry.
3. General theory of systems.
4. Physical Geometry.

**Remark:**

We do not need to include Chronology (*i.e.* the set of theories of time) in the background because time plays no role in Thermostatistics.

### 3.3 Primitive Basis

The conceptual space of the theory is spanned by the basis  $\mathbf{B}$  of primitive concepts, where

$$\mathbf{B} = \langle \Sigma, \overline{\Sigma}, \mathcal{F}, \Phi, S, U, Q \rangle.$$

The elements of this basis will be partially characterized by the axiomatics of the theory and the derived theorems. We shall class the axioms into three different classes: mathematical ( $\mathbf{M}$ ), physical ( $\mathbf{P}$ ) and semantical ( $\mathbf{S}$ ), according to their status in the theory.

### 3.4 Axioms

**Remark:**

The geometrical notions used below (mainly that of volume) are taken from the theory of physical geometry.

#### Group I: Systems and states

##### A 1 (Thermostatical systems)

[M]  $\Sigma, \overline{\Sigma}$  : *nonempty sets.*

[S]  $(\forall \sigma)_{\Sigma} (\sigma \stackrel{d}{=} \text{thermostatic system}).^4$

[S]  $(\forall \overline{\sigma})_{\overline{\Sigma}} (\overline{\sigma} \stackrel{d}{=} \text{environment of some thermostatic system}).$

##### A 2 (Properties)

[M]  $\mathcal{F}$  : *nonempty set.*

[S]  $(\forall F)_{\mathcal{F}} (F \stackrel{\wedge}{=} \text{property of the system}).$

##### A 3 (States)

[M]  $\Phi$  : *nonempty set of functions.*

[P]  $\forall (\sigma, \overline{\sigma})_{\Sigma \times \overline{\Sigma}}, (\exists \varphi)_{\Phi} / \varphi \stackrel{\wedge}{=} \mathbf{F}(\sigma, \overline{\sigma}).$

[S]  $(\forall \varphi)_{\Phi} (\varphi \stackrel{d}{=} \text{equilibrium state of the system}).$

**Remarks:**

1.  $\Sigma$  is the class of factual reference of Thermostatistics. A member  $\sigma \in \Sigma$  represents an arbitrary thermostatic system, for instance a body formed by other bodies (subbodies or subsystems) in interaction. In next subsection we will give a more accurate characterization of a thermostatic system.
2. Since to study a system it is necessary to conceptually isolate it from the surroundings, the objects that are not part of the system but interact with it in a noticeable way will be denoted by  $\overline{\sigma}$ . They will be called environment of the given thermostatic system and the set of all environments will be denoted by  $\overline{\Sigma}$ .

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<sup>4</sup>The symbol  $\stackrel{d}{=}$  is used here for the relation of denotation (see Ref. [16] for details).



3. **A3** gives a mathematical characterization of each  $F \in \mathcal{F}$  as a function that depends neither on space coordinates nor on time. Each  $F$  depends solely on the system and its environment, and has a subset of  $\mathfrak{R}$  as range. These properties need not be specified now. Since different systems usually require the specification of different properties, this approach is valid for different kinds of systems.
4.  $\mathcal{F}$  should not be confused with  $\mathbf{F}$ .  $\mathcal{F}$  denotes the set of all functions representing properties of any thermostatic system included in  $\Sigma$ .  $\mathbf{F}$  instead, denotes a list of all the functions representing properties of a given thermostatic system.
5. From the axioms given above we can identify the set  $M$  (see **D9**) as a subspace of  $\Phi$ . For instance  $M = (p, V)$  or  $M = (S, U)$  in the case of an ideal gas. (Cf. **A7** and **D21**, **D22**.)
6. Note that the set  $\Phi$  is the lawful state space of all systems in  $\Sigma$ , while  $S_L(\sigma)$  is the lawful state space of a particular system  $\sigma$ .
7. We shall see that the main goal of Thermostatistics is to predict the properties of a given system in an equilibrium state reached by means of some transformation  $g$  which started from a different equilibrium state. Moreover, it will be clear that a more detailed description is obtained when the value of a certain functional associated with each transformation can be established.
8. To avoid unnecessary complexity in the notation, the dependence of the quantities on the reference thing  $x_f$  (or the auxiliary set  $M$ ) will not be made explicit whenever possible.

Next we shall characterize the basic unit of the composition of any thermostatic system. In most cases, a thermostatic system is a composite system (commonly called heterogeneous system), and each of these components is a homogeneous system, called phase or elementary system. The components of a homogeneous system, if any, are not thermostatic systems. This suggests the following definition:

**D 18 (Elementary system)** *Any thermostatic subsystem such that none of their components is a system will be called elementary system (or phase). Formally:*

$$\sigma_i \stackrel{Df}{=} (\sigma_i)_\Sigma \wedge \forall x (x \in \mathcal{C}(\sigma_i) \Rightarrow x \notin \Sigma)$$

with  $\Sigma^* \subset \Sigma$ , the set of elementary systems.

**A 4 (Composition)** *The composition of an elementary system is given by the set of different chemical species present in it, that is to say:*

$$\mathcal{C}(\sigma_i) = \bigcup_{i=1, \dots, r} e_i$$

such that  $e_i$  is a chemical species. Thus,  $\sigma_i$  will be called elementary system or phase of  $r$  components.

**Remark:**

The concept of chemical species is taken from Chemistry, which is part of our material background.

**D 19 (Heterogeneous system)** *Every composite system formed by two or more elementary systems will be called heterogeneous.*

Note that in the previous definition the composition of each phase has not been mentioned. This will allow us to define the concept of a simple system. We know that every system may display a number of phases, and that every system of  $m$  phases can be transformed into another system of  $m'$  phases. Each of these phases may have the same or different composition. This motivates the following definition:

**D 20 (Simple system)** *We call simple system  $\sigma_i$  every elementary system and every heterogeneous system formed by elementary systems having the same composition. That is to say:*

$$\sigma_i = \sum_{j=1,\dots,m} \sigma_j, \text{ such that } \mathcal{C}(\sigma_j) = \bigcup_{l=1,\dots,r} e_l, \quad \forall j = 1, \dots, m.$$

*The system  $\sigma_i$  is called a simple system of  $m$  phases and  $r$  components.*

**Remark:**

Note that every elementary system is a simple system, but all simple systems are either elementary or a composition of them.

The tacit assumption of Thermostatistics is that each subsystem  $\sigma_i \in \Sigma^*$  is in equilibrium and has a number of properties that do not depend on the space coordinates. Accordingly, the formulation is global, because the properties are constant in each  $\sigma_i$ . Moreover, keeping in mind that each component of the state function  $\mathbf{F}$  represents a property of  $\sigma_i$ , we define:

**D 21 (Thermostatic coordinates)** *Each of the state coordinates of the function  $\mathbf{F}$  that represents a property of system will be called a thermostatic coordinate.*

In accordance with the definition of extensive properties we can adopt the following convention:

**D 22 (Generalized coordinates)** *The functions  $X$  that represent extensive properties will be called generalized coordinates. The set of all the generalized coordinates will be denoted by  $\mathbf{X}$ . Formally,*

$$(\forall X)_{\mathbf{X}} (\forall P)_{\mathcal{P}} (X \stackrel{\wedge}{=} P \wedge P \text{ is extensive}) , X \stackrel{Df}{=} \text{generalized coordinate}$$

**D 23 (Thermostatic configuration space)** *For every  $\sigma_i$ , the space spanned by the generalized coordinates is called the thermostatic configuration space and will be denoted by  $S(\sigma_i)$ .*

**Remarks:**

1. It must be noted that all the quantities that specify a state are time-independent. In particular, the properties of elementary systems are spatially and temporally constant. In particular, due to the requirement of spatial constancy, inhomogeneous fields (such as gravitational fields) are excluded from Thermostatistics.
2. The only states that Thermostatistics need are the equilibrium states introduced in **(A3)**. Consequently, properties are defined only for such states. This feature of Thermostatistics has been mistakenly extrapolated to Thermodynamics, where sometimes it is considered that properties are not defined for states far from equilibrium (For a discussion, see Ref. [2]). This misconception, inherited from operationism, is caused by the belief that properties are defined for the states in which it is possible to measure them. Moreover, we can draw no conclusions from Thermostatistics on this matter, because it deals only with equilibrium states.
3. **D23** identifies the conceivable state space of a system from the point of view of Thermostatistics as the thermostatic configuration space.
4. As a simple corollary of the above definitions, the conceivable state space of a composite system  $\sigma = \sigma_1 + \sigma_2$  is spanned by the Cartesian product  $S(\sigma) = S(\sigma_1) \times S(\sigma_2)$ .
5. The definition of a closed system w.r.t. the property  $P$  fixes the structure (*i.e.* the constraints) of the system. Let us consider for example a system built up of  $N$  subsystems, such that each of these is open regarding  $P_j \hat{=} X_j$ , but the composite system is closed regarding the same property. The following condition must be fulfilled:

$$\sum_j^N X_j = X^T = \text{constant}$$

where  $X^T$  is an invariant of the composite system for all possible transformations.

6. Note that we have not defined “reservoir”, “wall”, or “enclosure”. Such concepts are only necessary in formulations based on operationism. For example, a usual definition of closed system is a “system in an impermeable enclosure” [4].

The state coordinates are not independent of each other. This is clarified by the following definition:

**D 24 (Thermostatic degrees of freedom)** *We shall call thermostatic degrees of freedom ( $N$ ) the minimum number of independent state coordinates  $F_i$  that should be specified to determine univocally the equilibrium state of the system.*

We have characterized the systems and classified their properties in the equilibrium states. We consider next two other physical properties of the primitive base:

## Group II: Fundamental properties

### A 5 (Entropy)

[M]  $\forall(\sigma_i, \bar{\sigma}_i)_{\Sigma \times \bar{\Sigma}} (\exists S)_{\mathcal{F}}(S : \Sigma \times \bar{\Sigma} \rightarrow \mathbb{R}^+)$ .

[P]  $S \in \mathbf{X}$ .

[S]  $S(\sigma_i, \bar{\sigma}_i) \triangleq$  entropy of the system  $\sigma_i$  when it interacts with the environment  $\bar{\sigma}_i$ . Notation:  $X_0 \stackrel{d}{=} S$ .

### A 6 (Energy)

[M]  $\forall(\sigma_i, \bar{\sigma}_i)_{\Sigma \times \bar{\Sigma}} (\exists U)_{\mathcal{F}}(U : \Sigma \times \bar{\Sigma} \rightarrow \mathbb{R}^+)$ .

[M]  $U$  is a continuous, differentiable and monotonically growing function of  $S$ .

[P]  $U \in \mathbf{X}$ .

[S]  $U(\sigma_i, \bar{\sigma}_i) \triangleq$  internal energy of the system  $\sigma_i$  in the presence of  $\bar{\sigma}_i$ .

#### Remark:

Although these axioms refer to states and properties of simple systems  $\sigma_i$ , they can be extended to the more general case of composite systems. This extension is guaranteed by **A5** and **A6**, which assert that entropy and energy are extensive properties.

The equilibrium states are represented by the state function **F**. We now proceed to list the axioms that relate the independent properties of the system to those states. That is to say, we list the axioms that characterize both mathematically and physically the equilibrium states.

## Group III: Equilibrium states

### A 7 (Equilibrium representation)

[M] *The equilibrium states of every thermostatic system are completely specified by the generalized coordinates. This means that the state function is given by*

$$\mathbf{F} = \langle X_0, \dots, X_n, X_{n+1}, \dots, X_p \rangle,$$

*where the first  $n+1$  coordinates are independent and they determine the state of the system. The remaining  $p - n$  coordinates are dependent on the ones in the first group.*

### A 8 (“Second Law”)

[P] *For every closed composite system  $\sigma$ , the values taken by the independent generalized coordinates in the equilibrium state  $\varphi'$  are those that minimize the function  $U$  of the system, taking into account the values in the state  $\varphi$  with internal bonds.*

### A 9 (“Third Law”)

[P] *The entropy of any thermostatic system is null in the state for which  $(\frac{\partial U}{\partial X_0})_{X_1, \dots, X_n} = 0$ .*

**Remarks:**

1. **A7** is of fundamental importance because it states that equilibrium states are independent of each other. In other words, Thermostatistics studies only those systems in which the inherited changes are not contemplated. Also, it restricts the configuration space  $S(\sigma)$  since it assures the interrelation among dependent and independent coordinates.
2. The set of  $n+1$  independent coordinates in **A7** spans the auxiliary set  $M$  and introduces an implicit selection of the reference thing  $x_f$ .
3. In this representation, the internal energy is a dependent generalized coordinate. This means that it can be written as  $U = U(X_0, \dots, X_n)$ . Then **A8** settles the restriction that in any equilibrium state the form  $dU$  must be zero. That is to say,

$$\left(\frac{\partial U}{\partial X_j}\right) = 0 \quad j = 0, \dots, n.$$

We shall see below that the minimum condition leads to a classification of the equilibrium states regarding its stability.

4. **A8** and **A9** are usually called second and third principle of Thermodynamics, respectively.
5. **A8** refers to closed composite systems because Thermostatistics is concerned with the determination of the final state reached after reducing the number of bond relationships among subsystems (internal bonds).
6. Thermostatistics deals only with initial and final equilibrium states: there is no room in the theory for real processes because any process is nothing but a sequence of temporally ordered lawful states. Therefore, the kind of process that the theory deals with are fictitious processes, if only because it takes no time for them to happen. Let us remark that quasiequilibrium states or states that “differ infinitesimally” from equilibrium states are alien to Thermostatistics. This eliminates from the theory the quasistatic processes, present in almost every elementary introduction to Thermostatistics.
7. It follows from the previous remark that the concept of “irreversibility”, associated to real processes does not play any role in Thermostatistics. Also, the notion of a “spontaneous process” does not have any semantic content in the theory because time is absent from it.

Next we give some more definitions that will be useful in the following.

**D 25 (Fundamental equation)** *For every simple system  $\sigma_i$ , we will call fundamental equation in the energy representation the expression of the internal*

energy in terms of the remaining generalized coordinates of state, that is to say:  
 $U = U(X_0, \dots, X_n)$

**D 26 (Generalized forces)** For every simple system  $\sigma_i$ , we define the generalized force  $Y_j$  as

$$Y_j \stackrel{Df}{=} \left( \frac{\partial U}{\partial X_j} \right)_{X_0, \dots, X_n}.$$

In particular,  $Y_0$  will be denoted by  $T$  and will be called temperature:

$$T \stackrel{Df}{=} \left( \frac{\partial U}{\partial S} \right).$$

**Remark:**

Let us point out that temperature here is only a conventional name. We need a semantic postulate (or rule of correspondence) in order to confer some physical meaning to it.

**D 27 (Equation of state)** Every expression that gives the generalized forces in terms of the independent generalized coordinates  $Y_i = Y_i(X_0, \dots, X_n)$  will be called a state equation of the system.

**D 28 (Generalized work)** The generalized work  $W_j$  associated with the transformation  $g$  on  $S_L(\sigma_i)$  is given by the following integral:

$$W_j = \int_g Y_j dX_j.$$

**Remarks:**

1. It is not the goal of Thermostatistics to give the functional form of  $U$ . Therefore, the fundamental equation must be conjectured or perhaps taken from some other branch of Physics. Nevertheless, once its expression has been obtained, the formalism provides the means to obtain results that can be contrasted empirically.
2. The assumption that  $U$  would be a monotonically growing function of  $S$  can be written locally as  $\frac{\partial U}{\partial S} > 0$ , and globally as follows:

$$U(X_0'', \dots, X_n) \geq U(X_0', \dots, X_n), \quad X_0'' \geq X_0'.$$

3. Neither empirical temperature nor empirical entropy need to be defined in this axiomatization.
4. Depending on the type of system and on the choice of the representation, volume ( $V$ ), longitude ( $L$ ), surface ( $\Gamma$ ), magnetic moment ( $M$ ), electric charge ( $q$ ), and number of moles ( $N$ ) will be generalized coordinates. The corresponding generalized forces  $Y_i$  will be pressure ( $P$ ), traction ( $\tau$ ), superficial tension ( $\gamma$ ), intensity of magnetic field ( $B$ ), electromotive force ( $\varepsilon$ ), and chemical potential ( $\mu$ ). All these concepts are taken from theories in our background.

5. There are as many generalized forces as generalized coordinates. In other words, there are as many state equations as generalized state coordinates. For example, in the case of pure substances, we have the “pressure” and the “caloric” equations of state [20]. Not all of them, however, are independent.

We have defined the functional associated with the transformations  $g$  (see **D28**). To complete our axiomatics we must characterize an important functional in Thermostatistics (which represents the energy transfer among subsystems) and its relationship with the previously defined functionals:

#### Group IV: Energy transfer

##### A 10 (Temperature (“Zeroth Law”))

[S]  $T \stackrel{\wedge}{=} \text{system temperature.}$

##### A 11 (Heat)

[M]  $\forall(\sigma_i, \bar{\sigma}_i)_{\Sigma \times \bar{\Sigma}} (\forall g)_{G_L(\sigma_i)} (\exists Q)(Q : \Sigma \times \bar{\Sigma} \times G_L \rightarrow \mathbb{R}).$

[S]  $Q(\sigma_i, \bar{\sigma}_i, g) \stackrel{\wedge}{=} \text{heat exchanged between } \sigma_i \text{ and } \bar{\sigma}_i, \text{ associated with the possible transformation represented by the function } g. \text{ Notation: } W_0 \stackrel{d}{=} Q.$

##### A 12 (“First law”)

[P]  $\forall(\sigma_i, \bar{\sigma}_i)_{\Sigma \times \bar{\Sigma}} (\forall g)_{G_L(\sigma_i)}, \Delta U = Q + \sum_j W_j = \sum_{j=0 \dots n} W_j.$

##### Remarks:

1. **A11** characterizes heat as a form of energy transfer among the system and its environment, which depends on the transformation  $g$ . In other words, heat is interpreted just as another form of interaction between systems.
2. Note that there is no mention to measurements of any kind in the definition of heat.
3. **A12** represents the conservation of energy (usually called the first principle). It must be realized that this is a fundamental natural law, and consequently cannot be taken as a definition of heat, as is often stated [13, 3, 9, 20].

## 4 Theorems

In this section we will give some theorems that can be deduced from our axiomatic basis.

**D 29 (nth order homogeneous function)** *A function  $\phi$  of the set of independent variables  $(X_1, \dots, X_j)$  is homogeneous of nth order if it satisfies the following condition:*

$$\phi(\lambda X_1, \dots, \lambda X_j) = \lambda^n \phi(X_1, \dots, X_j).$$

where  $\lambda$  is an arbitrary real number.

**T 1 (Extensivity criterion)** *Every extensive property is a homogeneous function of first order, w.r.t the independent generalized coordinates,*

$$X(Y_i, \dots, Y_l, \lambda X_{l+1}, \dots, \lambda X_n) = \lambda X(Y_i, \dots, Y_l, X_{l+1}, \dots, X_n).$$

**Proof:**

From **D12** and **D29**.

**T 2 (Intensivity criterion)** *Every intensive property is a homogeneous function of order zero w.r.t. the independent generalized coordinates.*

$$Y(Y_i, \dots, Y_l, \lambda X_{l+1}, \dots, \lambda X_n) = Y(Y_i, \dots, Y_l, X_{l+1}, \dots, X_n)$$

**Proof:**

From **D12** and **D29**.

**T 3 (Euler)** *Every generalized coordinate  $X$  can be written as*

$$X = \sum_{i=1, \dots, n} X_i \left( \frac{\partial X}{\partial X_i} \right)_{X_j}, \quad j \neq i.$$

**T 4 (Euler theorem applied to the energy)**

$$U = \sum_{i=0, \dots, n} X_i Y_i.$$

**Proof:**

Set  $X = U$  in Euler's theorem, **T3**.

**T 5 (Positivity of  $T$ )**  $\forall (\sigma_i, \bar{\sigma}_i)_{\Sigma \times \Sigma} (\exists T)(T \geq 0)$ .

**Proof:**

It follows from the fact that  $U$  is an increasing function of  $S$ .

**T 6 (Subadditivity of  $U$ )** *The function  $U$  is subadditive. That is to say, for a composite system  $\sigma = \sigma_1 + \sigma_2$ ,*

$$U(\sigma, \bar{\sigma}) \leq U(\sigma_1, \bar{\sigma}_1) + U(\sigma_2, \bar{\sigma}_2),$$

*where  $\bar{\sigma}$  denotes the environment of the composite system in the new equilibrium state without bonds.*

**Proof:**

It follows from **A8**.

**T 7 (Convexity of  $U$ )**  *$U$  is a globally convex function; i.e. for any changes  $\Delta X_j$ :*

$$2U(X_0, \dots, X_n) \leq U(X_0 - \Delta X_0, \dots, X_n - \Delta X_n) + U(X_0 + \Delta X_0, \dots, X_n + \Delta X_n).$$

**Proof:**

It follows as a consequence of the subadditivity and extensivity of  $U$  [21].



**Remark:**

The mathematical properties of energy expressed by the above theorems play a fundamental rôle in Caratheodory-like axiomatizations.

**T 8 (Gibbs-Duhem)** *The variables associated to every system with fundamental equation  $U = U(X_0, \dots, X_n)$ , satisfy the following condition:*

$$\sum_{i=0, \dots, n} X_i dY_i = 0$$

**Proof:**

Compare the differential of the fundamental equation **D25** with Euler's theorem applied to the energy.

The following theorem settles the number of thermostatic degrees of freedom for a system composed by open subsystems with respect to matter exchange and not subjected to electric, magnetic or gravitational fields.

**T 9 (Phase rule)** *The number of thermostatic degrees of freedom of a system  $\sigma$  composed of  $m$  elementary systems  $\sigma_i$  in equilibrium and  $r$  components is  $\mathcal{N} = r - m + 2$ .*

**Proof:**

From the definitions of phase, component and thermostatic coordinates.

**Remark:**

Obviously in the general case of systems composed by subsystems that are open with respect to other properties,  $\mathcal{N}$  will be given by the nature of the system and by the number of bond relationships. That is to say, if  $n_v$  thermostatic coordinates are subjected to  $n_l$  bonds relationships,  $\mathcal{N}$  will be given by  $\mathcal{N} = n_v - n_l$ .

Since the function  $U$  of a composite system can have several minima, we can give a classification of the different equilibrium states keeping in mind that the condition of minimum of **A8** can be local or global:

**T 10 (Equilibrium criterion)** *Consider a closed composite system with fundamental equation  $U = U(X_0, \dots, X_n)$ . The equilibrium state  $\varphi'$  is a local minimum if  $d^2U > 0$  at  $\varphi'$ . This is satisfied if and only if the Hessians at  $\varphi'$  are positive, that is to say:*

$$H_j > 0 \text{ for } j = 0, \dots, n.$$

**T 11 (Global equilibrium criterion)** *Consider a closed composite system with fundamental equation  $U = U(X_0, \dots, X_n)$ . The equilibrium state  $\varphi'$  is a global minimum or not according to the convexity of the function  $U$  at  $\varphi'$ .*

**Proof:**

Follows from **A8**.

**D 30 (Classification of the equilibrium states)**

1. An equilibrium state  $\varphi'$  will be called *stable* iff  $dU = 0$ ,  $d^2U > 0$  and **T11** is satisfied.
2. An equilibrium state  $\varphi'$  will be called *metastable* if  $dU = 0$ ,  $d^2U > 0$  and if **T11** is not satisfied.
3. A equilibrium state  $\varphi'$  will be called *critical* if  $dU = 0$ ,  $d^2U = 0$  and it satisfies **T11**.
4. A equilibrium state  $\varphi'$  will be called *unstable* if  $dU = 0$ ,  $d^2U < 0$ .

**Remark:**

In the previous classification, the first three cases belong to  $S_L(\sigma)$ , while the unstable equilibrium states are beyond the scope of Thermostatics.

Up to now we have been working with a functional model  $b = \langle M, \mathbf{F} \rangle$  where the components of  $\mathbf{F}$  were all generalized state coordinates. That is to say, whenever we use the fundamental equation  $U$ , we work in the so called *energy representation*. It is possible to rewrite the results in any other representation that uses generalized coordinates and generalized forces (or only generalized forces) by means of a change of representation.

**T 12 (Change of representation)** *Given a simple system  $\sigma_i$  with fundamental equation  $U(X_0, \dots, X_n)$ , it is possible to represent the system by means of a function  $R(X_0, \dots, X_l, Y_{l+1}, \dots, Y_n)$  in order to obtain an equivalent representation of the original one, by means of the following Legendre transformation:*

$$U = \langle M, \mathbf{F} \rangle \rightarrow f(U) = \langle M', f(\mathbf{F}) \rangle,$$

$$U = U(X_0, \dots, X_n) \rightarrow f(U) = R(X_0, \dots, X_l, Y_{l+1}, \dots, Y_n) = U - \sum_{j=l+1, \dots, n} X_j Y_j,$$

such that

$$\left( \frac{\partial R}{\partial X_i} \right) = Y_i, \quad i = 0, \dots, l,$$

$$\left( \frac{\partial R}{\partial Y_i} \right) = -X_i, \quad i = l+1, \dots, n.$$

**T 13 (Equilibrium condition in an arbitrary representation)** *The potential  $R$  is a convex function of the generalized coordinates and a concave function of the generalized forces.*

**Proof:**

See Ref. [22].

**Remarks:**

1. The function  $R$  in the new state coordinates will be called *thermodynamic potential*.
2. This theorem warrants that under any change of representation, the equilibrium states will be completely specified by  $l+1$  generalized coordinates and by  $n-l$  generalized forces.

3. The  $n$  generalized forces conjugated to the  $n$  generalized coordinates form a total of  $n$  couples  $(X_i, Y_i)$  whose product has energy dimensions. All the possible combinations of state coordinates, taking one of each conjugated couple, is equal to  $2^n$ . That is to say, in a system with  $n$  coordinates we can choose among  $2^n$  thermodynamic potentials.
4. **T13** extends the condition of stability to other representations.

**D 31 (Phase transition)** *Let  $\sigma$  be a system with thermodynamic potential*

$$R(X_0, \dots, X_l, Y_{l+1}, \dots, Y_n).$$

*Whenever some discontinuity exists in one or more first derivatives of  $R$ , we say that  $\sigma$  undergoes a phase transition.*

**D 32 (Continuous phase transition)** *Let  $\sigma$  be a system with thermodynamic potential  $R(X_0, \dots, X_l, Y_{l+1}, \dots, Y_n)$ . Whenever the first derivatives are continuous but the second derivatives of  $R$  are discontinuous or infinite, we say that  $\sigma$  undergoes a continuous phase transition.*

**T 14 (Maxwell relations)** *For every system with thermodynamic potential*

$$R(X_0, \dots, X_l, Y_{l+1}, \dots, Y_n),$$

*the following conditions are satisfied:*

$$\begin{aligned} \frac{\partial X_j}{\partial Y_k} &= \frac{\partial X_k}{\partial Y_j} \quad j, k \leq l, \\ \frac{\partial X_j}{\partial X_k} &= -\frac{\partial Y_k}{\partial Y_j} \quad j \leq l, k > l, \\ \frac{\partial Y_j}{\partial X_k} &= \frac{\partial Y_k}{\partial X_j} \quad j, k > l, \end{aligned}$$

*where all the variables  $X_0, \dots, X_l, Y_{l+1}, \dots, Y_n$  remain constant except the variable which is being differentiated.*

**Proof:**

From the equality of the mixed second derivatives of the thermodynamic potential  $R$ .

**Remark:**

Maxwell's relations (**T14**) define a symplectic structure on the state space of a thermostatic system, whose fundamental form is [23]:

$$\theta = dU - \sum_j Y_j dX_j = \delta Q$$

the last member being a usual notation for “infinitesimal heat transfer”. We see then that this geometric structure, which is basic in Carathéodory-like formulations, is secondary in our axiomatics.

## 5 Discussion

We have given an axiomatic presentation of Thermostatistics that is realistic and objective. One of the effects of the assumption of a realistic ontology is the complete absence of definitions that (inconsistently) appeal to measurements in our axiomatizations. Also, many of the basic concepts that are presupposed by other axiomatizations have been specified here (*e.g.* those of system, subsystem, environment, state, etc).

The conceptual space of the theory is generated by a 7-tuple in which the set of systems is the unique factual reference. The other primitive elements are concepts of two types. The first type are properties (or groups of properties) of systems. The second type are those associated with the interaction of systems with the environment. These fundamental properties that are part of the primitive basis are entropy, internal energy and heat (introduced here as an interaction). They allow us to define Thermostatistics (and maybe Thermodynamics too) as the science of heat and temperature, which is in this axiomatization a defined concept. Equilibrium states have also been introduced as primitives, since Thermostatistics deals with this sole class of states. This entails that properties are necessarily defined for this states, but it does not mean that they cannot be extended for non-equilibrium states, such as those studied by Thermodynamics.

It is also clear from our axioms that Thermostatistics deals neither with processes nor with generalizations of them (like the quasistatic processes, originally defined as *infinitely small changes of system carried out at infinitely large time, to allow the system to be in equilibrium in all instants of time*).

Most of present-day axiomatizations incorporate concepts that have no room in a realistic philosophy of science. Among others, we can cite those of “empirical temperature”, “empirical entropy”, “partitions” and “enclosures” (used to characterize the connection among subsystems). Note that we have not introduced neither empirical definitions nor experimental devices to justify them. However, these should be consistent with the definitions given here.

The concept of heat was introduced here in accordance with historical tradition [15] and with the definitions implicit in the usual methods of calorimetry. The introduction of definitions and axioms in the present formulation has been guided by empirical knowledge, but they have no logical or epistemological dependence on it. The reverse is true: the design of experiment (and of technological devices) is guided by the theories (or, at least, theoretical hypotheses) that are being tested (or applied).

Let us remark that formalizations based on Caratheodory’s approach do not offer an improvement on the understanding of the entropy concept. The assignment of *properties* to the state space does not provide a deepening of the concepts, but (perhaps) a deepening into the mathematical foundations. To achieve understanding (which is a psychological category) it is necessary to give an explanation (epistemological category) that involves some physical mechanism of interaction (ontological category). Because of its very nature, no mechanism is assumed in Thermodynamics, except that of heat exchange. Indeed, Thermostatistics is a very versatile theory because it is an example of a *black box theory*. That is to say, no hypothesis is made about the internal mechanisms acting in the system under study. The relationship among observational variables is structural since the interaction mechanism is at the level of systems, and therefore we can ignore the particular internal details. These are

left to deeper theories like statistical mechanics. In this way, depth is achieved by conjecturing some interaction mechanism and testing its consequences.

However, given its extreme generality, the theory cannot be put to the experimental test. (The same holds for any other hypergeneral theory, such as Hamiltonian dynamics and general field theory.) To test the theory we must enrich it with a set of constitutive equations (such as the ideal gas law) that specify the nature of the “stuff” (or matter) that the system of interest is made of. But of course, such enrichment (or specialization) goes beyond the foundations of physics, which is only concerned with the entire genera of physical things.

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